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Aerobic Oxidation of Cyclohexane Catalyzed by Size-Controlled Au Clusters on Hydroxyapatite: Size Effect in the Sub-2 nm Regime

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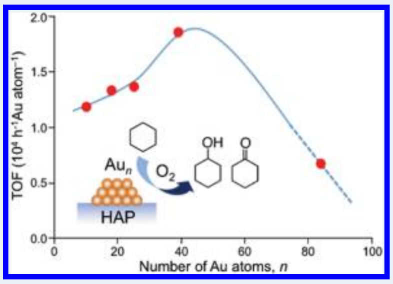
S *Supporting Information*

ABSTRACT: In this work, we synthesized gold clusters, Au_n (n = 10, 18, 25, 39), with atomically controlled sizes on hydroxyapatite (HAP) and studied the catalysis for aerobic oxidation of cyclohexane. These Au_n/HAP catalysts could efficiently oxidize cyclohexane to cyclohexanol and cyclohexanone. The turnover frequency monotonically increased with an increase in the size, reaching values as high as 18 500 h^{-1} Au atom^{-1} at $n = 39$, and thereafter decreased with a further increase in n up to $n \sim 85$. This finding provides a fundamental insight into size-specific catalysis of gold in the cluster regime (diameter < 2 nm) and a guiding principle for rational design of Au cluster-based catalysts.



KEYWORDS: Au clusters, size effect, aerobic oxidation, hydroxiapatite

Gold nanoparticles (AuNPs) on solid supports have been studied extensively as promising catalysts for a variety of oxidation reactions. In particular, increased interest has been focused on using O_2 as an oxidant, from the viewpoint of green chemistry.[1−6] Extensive studies have revealed that the size (diameter) of AuNPs has a significant influence on their catalytic properties: the catalytic activity increases with decreasing size.[7,8] However, fundamental questions remain unanswered: How does the catalytic activity evolve in the cluster regime (diameter < 2 nm), and how does the catalytic activity correlate with that of single Au atoms?[9,10] To answer these questions, it is essential to synthesize a series of Au_n clusters with atomically controlled sizes of n (number of Au atoms) on solid supports. Soft landing of size-selected, bare Au_n clusters onto supports is a straightforward method, but requires sophisticated equipment; a mixture of Au_{6-10} has been successfully immobilized on TiO_2 and Al_2O_3 using this method.[11] Diameter-controlled AuNPs have been synthesized by removing the ligands from monodisperse AuNPs that are protected by ligands (thiolates/phosphines) on supports.[12−15] This approach has been successfully applied to the synthesis of size-controlled Au_n clusters (Au_{55} on silica,[16] Au_{11} on mesoporous silica (SBA-15),[17] and Au_{25} on hydroxyapatite (HAP).[18]); however, to the best of our knowledge, systematic studies on the size effect on the catalysis in the sub-2 nm region have not been conducted so far.

The aim of the present work is to develop the size-controlled synthesis of Au_n clusters on solid supports and to reveal the effect of cluster size on catalysis in aerobic oxidation in the sub-2 nm region. To this end, we utilized a series of glutathione (GS)-protected Au_n clusters with well-defined size n as Au precursors.[19] HAP ($Ca_{10}(PO_4)_6(OH)_2$) was used as the support[20−22] with the expectation that $Au_n(SG)_m$ passivated by tripeptide molecules (glutathionates) are adsorbed as efficiently as other biomolecules via hydrogen bonding and/or electrstatic interaction.[23] The catalytic activities of the size-selected Au_n clusters on HAP were compared for examining their use in the aerobic oxidation of cyclohexane, which is industrially important because the products, cyclohexanone and cyclohexanol (Ketone/Alcohol or KA-oil), are key intermediates for the production of nylon-6 and nylon-66, but remains a challenge in modern chemistry.[24] We hope that this work will deepen understanding of the intrinsic size effect of gold catalysis and provide a guiding principle to design Au cluster-based catalysts.

Size-controlled Au_n clusters on HAP were synthesized in two steps. The first step was adsorption of $Au_n(SG)_m$ with well-defined compositions on HAP to produce the composite $Au_n(SG)_m$/HAP. As Au precursors, we selected $Au_n(SG)_m$ with (n, m) = (10, 10), (18, 14), (25, 18), and (39, 24); the $Au_{18}(SG)_{14}$ and $Au_{25}(SG)_{18}$ samples were chemically pure, whereas the $Au_{10}(SG)_{10}$ and $Au_{39}(SG)_{24}$ samples were contaminated with a small amount of $Au_{11}(SG)_{11}$/$Au_{12}(SG)_{12}$ and $Au_{38}(SG)_{24}$, respectively.[19] The second step was calcination of the $Au_n(SG)_m$/HAP composites to remove the GS ligands.[18,25] The resulting catalysts are hereafter referred to as Au_n/HAP.

The $Au_n(SG)_m$/HAP composites were obtained by filtration of the mixture of HAP and $Au_n(SG)_m$ in basic water (pH ∼ 9.8). The filtrates were colorless, indicating complete adsorption of $Au_n(SG)_m$ on HAP (Figure S1 of the Supporting Information). The amount of Au adsorbed is estimated from the molar extinction coefficient[19] to be 0.2 wt % with respect to that of HAP. The reflectance spectra of $Au_n(SG)_m$/HAP exhibited profiles similar

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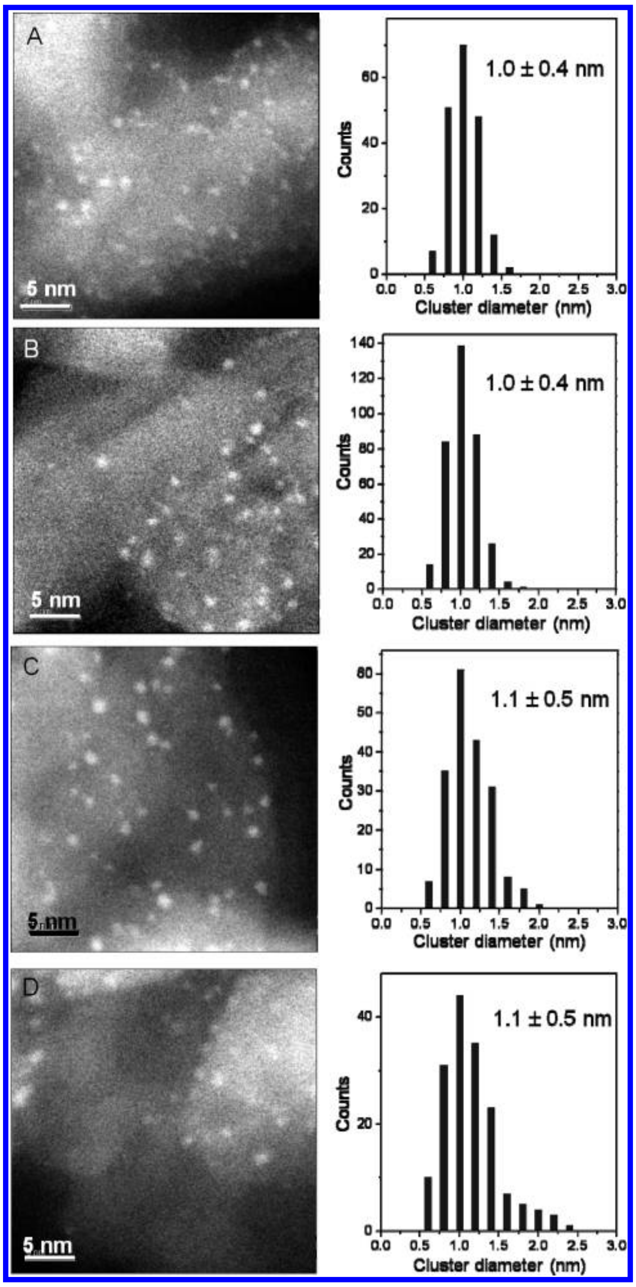


Figure 1. Representative HAADF-STEM images of Au_n/HAP and cluster size distributions; the n values are (A) 10, (B) 18, (C) 25, and (D) 39.

to the absorption spectra of $Au_n(SG)_m$ (Figure S2 of the Supporting Information).[19] This result indicated that $Au_n(SG)_m$ were adsorbed on HAP with their form intact. The following improvements were made to the preparation method of $Au_n(SG)_m$/HAP[18] to minimize the possibility of aggregation of Au clusters during the calcination: (1) The surface area of HAP was increased from 20−30 to ~100 $m^2\ g^{-1}$ (Table S1 of the Supporting Information) using the synthesis method given in ref 26. (2) The Au loading was reduced from 0.5 to 0.2 wt %. (3) The pH of the dispersion was set ~9.8 higher than the pK_a values (2.12, 3.53, 8.66, 9.12) of GSH (Figure S3 of the Supporting Information). These improvements reduced the density of adsorbed $Au_n(SG)_m$ and allowed them to be adsorbed more homogeneously over the HAP support through the electrostatic repulsion between the carboxylate moieties[27] of the GS ligands.

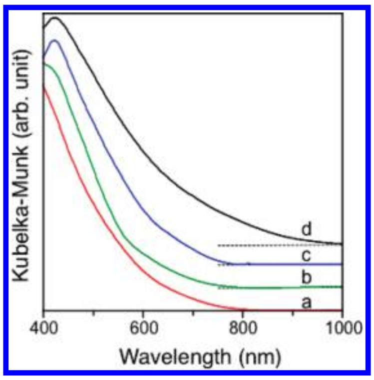


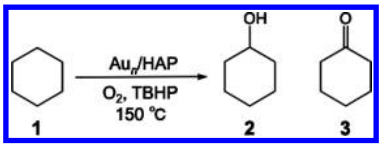
Figure 2. Diffuse reflectance UV−vis spectra of Au_n/HAP; the n values are (a) 10, (b) 18, (c) 25, and (d) 39.

The Au_n/HAP catalysts were prepared by calcinating the $Au_n(SG)_m$/HAP composites at 300 °C for 2 h in vacuo.[18] The effective removal of the GS ligands was confirmed by inductively coupled plasma (ICP) analysis and X-ray photoelectron spectroscopy (XPS). The sulfur content in $Au_{25}(SG)_{18}$/HAP (58 ppm), for example, was reduced to 5 ppm in Au_{25}/HAP, which was comparable to the amount of sulfur impurity in HAP. Preliminary XPS measurement on $Au_{25}(SG)_{18}$/HAP and Au_{25}/HAP (data not shown) also showed that the sulfur content after the calcination is negligibly small. Au loading was confirmed to be 0.17−0.21 wt % by the analysis (Table S1). Calcination under the conditions mentioned above did not alter the structure of the HAP (Figure S4 of the Supporting Information).

Transmission electron microscopy (TEM) on Au_n/HAP revealed no appreciable aggregation of the Au clusters during the calcination. Figure 1 shows typical high angle annular dark field-scanning TEM (HAADF-STEM) images and size distributions for Au clusters obtained by counting more than 160 particles. The average diameters (d_{av}) of the Au clusters in Au_n/HAP for $n = 10, 18, 25, 39$ appeared to be 1.0−1.1 nm, regardless of the size of the $Au_n(SG)_m$ precursors. Similar results were also obtained by the conventional TEM observation (Figure S5 of the Supporting Information). Although neither HAADF-STEM nor TEM could differentiate the cluster size among the four Au_n/HAP samples, as anticipated from the spatial resolutions of these methods, we can conclude that the aggregation of Au clusters during the calcination is negligible. A direct method to probe the number of Au atoms in each cluster is to analyze the contrast of the individual clusters in the HAADF-STEM images,[28,29] which is a subject of our future study. Instead, we compared the optical spectra of Au_n/HAP composites (Figure 2). The spectra show different profiles, and the optical onset for $n = 39$ is located at notably-longer wavelength than the others. These observations indicated that the Au clusters of Au_n/HAP were composed of different numbers of atoms.

Although the results in Figures 1 and 2 suggest that the size of the Au clusters is preserved during the calcination, the distributions of the diameters are broader and the optical spectra are smoother than those expected for single-sized Au clusters. We believe that these observations are partly accounted for in the formation of structural isomers of the Au clusters. An ensemble of structural isomers produced in the calcination of $Au_n(SG)_m$ will give rise to polydisperse TEM images and smooth optical spectra because the spectral profiles may vary among the isomers. Strong interaction between the Au and PO_4^{3-} moieties[30] of HAP additionally contributes to the modification of the structures of the Au clusters.

Table 1. Oxidation of Cyclohexane[a]



entry	catalyst	conv (%)[c]	selectivity (%)[b] 2	selectivity (%)[b] 3	TOF ($\times 10^4$ h^{-1})[d]
1	Au_{10}/HAP	11.6	58	41	1.19
2	Au_{18}/HAP	12.9	49	50	1.33
3	Au_{25}/HAP	14.2	50	49	1.37
4	Au_{39}/HAP	14.9	50	49	1.85
5	$Au_{\sim 85}$/HAP	6.7	53	41	0.68
6	Au_{25}/HAP$_{second}$	13.9	51	47	
7	Au_{25}/HAP$_{third}$	13.7	50	48	

[a] The reactions were carried out with Au$_n$/HAP (100 mg) and TBHP (10 mg) in **1** (10 mL) under an O_2 atmosphere (1 MPa, ~30 mL) at 150 °C for 4 h. [b] Selectivity was determined as the ratio of the yield of each product to the total yield of products. [c] Conversion was calculated on the basis of the amount of **1** recovered. [d] TOF was calculated from the amount of **1** recovered for the following reaction conditions and materials: Au$_n$/HAP (100 mg), TBHP (10 mg), **1** (15 mL), and O_2 (1 MPa, ~100 mL) at 150 °C for 30 min.

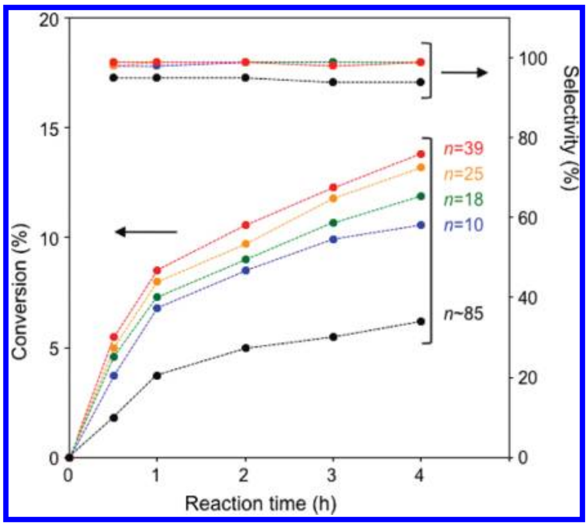


Figure 3. Time dependence of the conversion of **1** and the total selectivity of **2** and **3** by Au$_n$/HAP. The reactions were carried out with Au$_n$/HAP (100 mg) and TBHP (10 mg) in **1** (15 mL) under an O_2 atmosphere (1 MPa) at 150 °C. During the reaction, the O_2 gas was continuously supplied from the gas cylinder to keep the pressure constant.

Aerobic oxidation of cyclohexane (**1**) catalyzed by AuNPs (d_{av} > 3 nm) supported on various supports has been studied by several groups.[31−37] We investigated how the catalytic activity of Au$_n$/HAP (n = 10, 18, 25, 39) evolves in the size range d_{av} < 2 nm using this reaction as a test reaction. As a reference, we also studied the catalysis of larger Au clusters (d_{av} = 1.4 ± 0.6 nm, 0.2 wt % of Au) on HAP prepared by a conventional adsorption method (Figures S6 and S7 of the Supporting Information). This catalyst is referred to as $Au_{\sim 85}$/HAP because the average diameter of the Au clusters corresponds to that of Au_{85} on the assumption that the clusters have the same density as bulk Au.

Table 1 summarizes the catalytic performance of Au$_n$/HAP for the oxidation of **1** under an O_2 atmosphere (1 MPa) at 150 °C. No conversion was observed in the absence of gold, which confirms that the Au clusters play an essential role in the catalytic conversion. The addition of a small amount of TBHP ([TBHP]/[**1**] = 1.2×10^{-3}) was essential to initiate the reaction,[34] suggesting that this oxidation proceeds via a complex radical chain mechanism.[24,37] In all the cases, cyclohexanol (**2**) and cyclohexanone (**3**) were obtained as the primary products with nearly equivalent yields; adipic acid was not formed. The conversion of **1** after 4 h gradually increased from 11.6% to 14.9% for the increase in n from 10 to 39 (entries 1−4) and decreased to 6.7% for $n \sim 85$ (entry 5). To check the lot-to-lot reproducibility of the results, we tested the catalytic activity for three Au_{25}/HAP catalysts synthesized independently. The conversions observed for each of the catalysts were similar with a typical standard deviation of less than 1% (Table S2 of the Supporting Information). This result clearly shows *how a difference in cluster size of several atoms affects the catalytic activity.* The Au$_n$/HAP catalysts could be reused at least three times without any noticeable loss in activity (entries 3, 6, 7). The recyclability is ascribed to the durability of the Au$_n$/HAP catalysts under the conditions as evidenced by the optical spectra (Figure S8 of the Supporting Information) and TEM images (Figure S9 of the Supporting Information) of Au_{25}/HAP before and afer the catalytic usage.

We studied the catalytic behavior of Au$_n$/HAP in more detail under a constant pressure (1 MPa) of O_2, since most of the O_2 in the autoclave was consumed after 4 h under the conditions employed above (Table 1). Figure 3 shows time dependence of the conversion of **1** and total selectivity for **2** and **3** (KA-oil) by Au$_n$/HAP. Conversions increased with a reaction time for all the catalysts. The total selectivities for **2** and **3** were nearly constant, regardless of the conversion, in sharp contrast to the results reported in refs 34 and 36. The selectivities for KA-oil were as high as ~99% for smaller Au$_n$/HAP (n = 10−39), whereas it was reduced slightly to ~95% for $Au_{\sim 85}$/HAP. The selectivities for Au$_n$/HAP (n = 10−39) are among the highest in the literature: 92−97% for Au (>2 nm)/MCM-41,[32] 94−96% for Au (2.8, 6.5, 8.8 nm)/SBA-15,[33] 10−23% for Au/graphite,[34] 84−87% for Au (3−6 nm)/Al_2O_3,[35] 92% for Au (3−8 nm)/TiO_2/SiO_2,[36] 65% for Au (~5 nm)/TiO_2,[37] 60% for Au (~5 nm)/Al_2O_3,[37] and 71% for Au (~4 nm)/SBA-15.[37]

The time evolution of the conversion shown in Figure 3 indicates that the activities increased in the order of $Au_{\sim 85} < Au_{10} < Au_{18} < Au_{25} < Au_{39}$. The catalytic activities of Au$_n$/HAP were compared more quantitatively by using the TOF values, which is defined as the number of molecules of **1** converted per Au atom per hour.[31−36] The TOF values were tentatively calculated from conversions at the initial stage of the reaction (0.5 h). The TOF values of Au$_n$/HAP thus obtained are listed in Table 1. They are comparable to or higher than those of Au catalysts reported previously (11214 h^{-1} for Au (>2 nm)/MCM-41[32] and 16136 h^{-1} for Au (3−6 nm)/Al_2O_3[35]) but smaller than the highest value in the literature, which amounts to 40 133 h^{-1} for Au (3−8 nm)/TiO_2/SiO_2.[36] Figure 4 shows a plot of the TOF values as a function of the cluster size, n. The TOF values monotonically increase with an increase in the size in the n range from 10 to 39 but decrease in the n range from 39 to ~85. Figure 4 reveals that there is an optimal size of Au clusters in the n range of 40−80 for

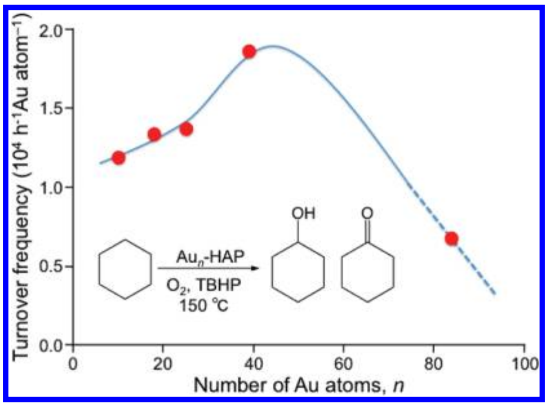


Figure 4. TOF values as a function of the cluster size n. The curve is a guide for the eye.

the aerobic oxidation of cyclohexane. Although it is not clear at this moment how the Au clusters are involved in the complex oxidation processes, the volcano-shaped size dependence in Figure 4 cannot be explained solely in terms of geometrical factors, such as the surface area and density of low-coordination sites on Au clusters. The highest catalytic activity observed in the case of Au_{39} may be associated with their unique electronic structures, as suggested by the clear difference in the spectral onsets (Figure 2).

In summary, we have successfully synthesized a series of Au_n clusters with well-defined sizes on HAP. The catalytic properties of these ultrasmall Au_n clusters were investigated by examining their use in the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone under solvent-free conditions with O_2 as the oxidant. The total selectivity for cyclohexanol and cyclohexanone reached ~99%, affording a cyclohexane conversion exceeding 10%. The optimal size of Au_n clusters for the aerobic oxidation was determined to correspond to the n range 39−85.

EXPERIMENTAL METHODS

Preparation of Catalysts. GS-protected Au clusters $Au_n(SG)_m$ with (n, m) = (10, 10), (18, 14), (25, 18), (39, 24) were prepared according to a protocol previously reported by us.[19] HAP was prepared using the synthesis method given in ref 26. The $Au_n(SG)_m$ clusters (containing 2 mg Au) were dissolved in water (100 mL), which was adjusted to pH ~ 9.8 using diluted ammonia solution. The mixture was then stirred with HAP (1 g) for 4 h at room temperature. The $Au_n(SG)_m$/HAP composite was collected by filtration and then calcined in vacuo at 300 °C for 2 h to produce Au_n/HAP. Larger Au clusters ($d_{av} = 1.4 \pm 0.6$ nm, 0.2 wt % of Au) on HAP were prepared by a conventional adsorption method (Figures S6 and S7). If the Au clusters are assumed to have the same density as bulk Au, the average diameter corresponds to that of $Au_{\sim 85}$. Thus, this catalyst is referred to as $Au_{\sim 85}$/HAP, although the Au cluster size is not atomically controlled. The Au_n/HAP catalysts were characterized by reflectance optical spectroscopy, powder XRD, HAADF-STEM, TEM, N_2 adsorption/desorption isotherm, and ICP.

Catalytic Test. The catalytic performance of Au_n/HAP (n = 10, 18, 25, 39, ~85) for the aerobic oxidation of **1** was studied under solvent-free conditions. Typically, 100 mg of the Au_n/HAP catalysts (containing ~0.2 mg of Au, Table S1) and 10 mg of *tert*-butyl hydroperoxide were added to **1** (10 mL) in a Teflon tube placed in a stainless steel autoclave with an internal volume of 30 mL. After O_2 (1 MPa) was charged, the reaction mixture in the autoclave was incubated at 150 °C under stirring. After 4 h, the reaction mixture was filtered, and the filtrate was diluted with AcOEt. The chemical identity and the yield of the products were determined by gas chromatography.

ASSOCIATED CONTENT

Ⓢ Supporting Information. The preparation and characterization of $Au_n(SG)_m$, HAP, and Au_n/HAP. This information is available free of charge via the Internet at http://pubs.acs.org.

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